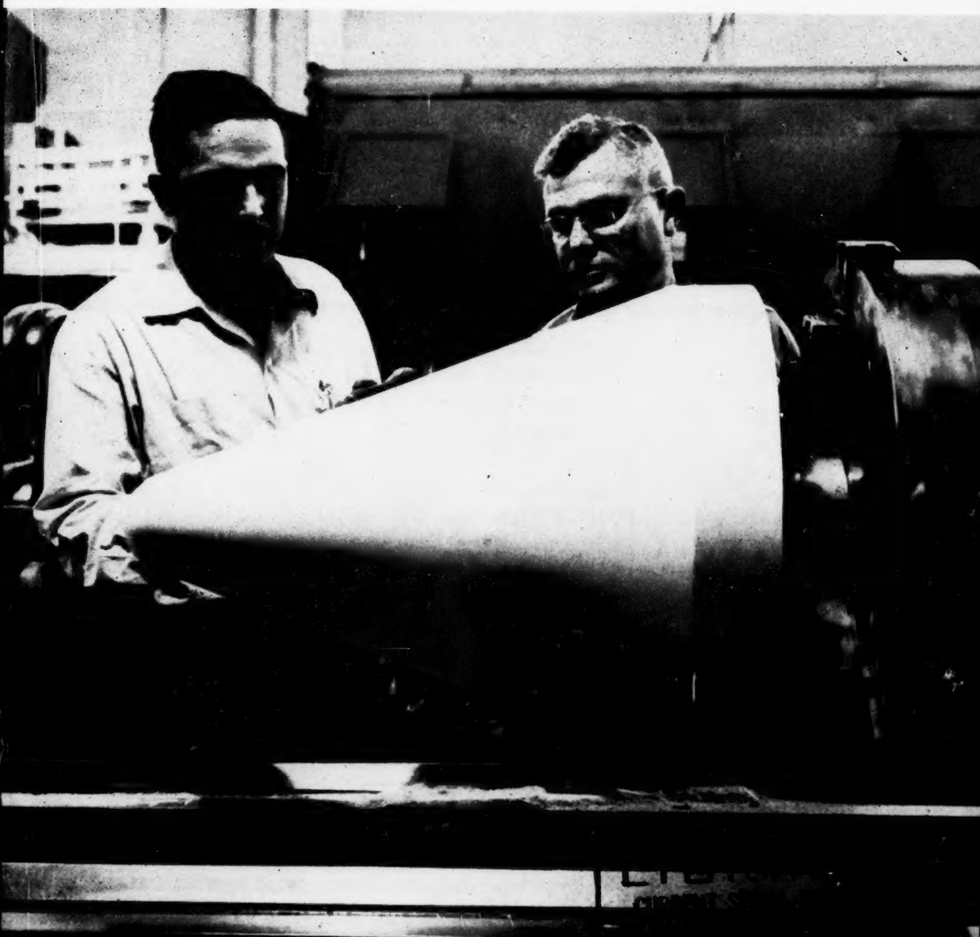
DECEMBER, 1958

The Research Engineer

Published by the Georgia Tech Engineering Experiment Station



Follow-up Ceramics Report

The Research Engineer

VOLUME 13, NO. 5 DECEMBER, 1958

Published 5 times a year by the Engineering Experiment Station
Georgia Institute of Technology, Atlanta, Georgia

contents

the cover

Research Engineer Nick Poulos, right, and machinist Fred Shue, check over a plaster model of a rocket nose cone in the Machine Shop of the Georgia Tech Engineering Experiment Station. The models made in Tech's machine shop are used by Poulos and his associates in making molds for the ceramic nose cone fabrication operation now going on in the laboratories of Tech's Ceramics Branch. For more about the operations of the Ceramics Branch turn to page 4.

The cover and all photographs in this issue by Bill Diehl, Jr.

THE RESEARCH ENGINEER is published five times a year in Feb., Apr., June, Oct. and Dec. by the Engineering Experiment Station, Georgia Institute of Technology. Entered as second-class matter September 1948 at the post office at Atlanta, Georgia under the act of August 24, 1912. Acceptance for mailing at the special rate of postage provided for in the act of February 28, 1952. Section 528, P.L.&R., authorized on October 18, 1948.

The President's Page

CERAMICS RESEARCH at Georgia Tech is an excellent example of how one well-planned campus program can serve several different areas of education, industry and government.

Every one of the full-time research personnel in this group (the Ceramics Branch) is a graduate of Tech's own School of Ceramic Engineering. Dr. Lane Mitchell, director of this school, and his staff are doing a fine job of educating their students, preparing them for contributions in both the industrial and research fields. In turn, the research branch provides part-time research work to some 20 undergraduate students from the Schools of Ceramic Engineering, Chemical Engineering, Mechanical Engineering and Industrial Engineering. This work adds much valuable experience to the students' scholastic work as well as aids them financially.

As a research facility for Georgia's most important mineral, clay, the Ceramics Branch is also making early contributions to Tech's new minerals development program for the State. Research into new uses for Georgia's unique deposits of high-grade clays is one of the best ways to support the program's goal—the development of Georgia's mineral resources for an expanded and better-balanced State economy.

Already, applications of ceramic materials to the special high-temperature and radiation conditions of reactor operation are being studied here, and research in this area is expected to become an important complement to the nuclear science program at Tech.

As the following articles testify, the effectiveness of this broad program is easily measured by the outstanding graduates, the added fundamental knowledge in the field, new products, and important contributions to national defense.

E. D. Harrison

President

THE CERAMICS BRANCH

by J. D. Walton, Head, Ceramics Branch

THE CERAMICS BRANCH of the Engineering Experiment Station was formed one year ago and a review of its activities at that time was presented in *The Research Engineer*. This issue will serve as a progress report on the work being continued as well as a report on new projects which have been initiated during the past year.

In the summer of 1957, the ceramic research group occupied laboratories which consisted of some 1500 to 2000 square feet of floor space. In the fall of the same year, new facilities were made available in a less congested area which allowed us to set up our rocket motor. This facility provided some 3500 square feet of office and laboratory space. There is presently being constructed an addition to our laboratory which will be used exclusively for slip casting and plaster mold work and will increase our

Ceramics Branch Head J. D. Walton conducts a staff meeting of the Branch's senior members: L to R are Joe Harris, Bill Teague, Nick Poulos, Walton, Bill Zenoni, Steve Fuller and Mac Bowen. Not present were staff members J. D. Fleming and C. R. Mason.

The past and the future are linked by the work of this group of thirty young researchers in a field almost as old as man

working area by an additional 1000 square feet.

During this same period of time, the number of employees of the Ceramics Branch rose from 15 to the present number of 30, of which approximately half are full-time employees, including nine graduate engineers. Part-time employees consist wholly of graduate and undergraduate students representing the Ceramic Engineering, Chemical Engineering, Mechanical Engineering and Industrial Engineering Schools at Georgia Tech.

Last year, the project budget of the Ceramics Branch was approximately $130,000. Our goal of doubling the work within a year has been more than realized with a current project budget of $300,000. This rapid growth reflects not only the increasing demand of the military for materials which will perform at higher and higher temperatures, but also the expanding facilities being put into operation by the Ceramics Branch which allow Georgia Tech to offer a greater diversification of services to those desiring research in the high temperature materials field.

It was with a great deal of enthusiasm that we began work on the 15th of November on our first AEC contract. During the past year, it was a very specific goal of our group to expand its activities to include the study of ceramic materials for nuclear applications, and under this contract, we will study fused silica for such applications.

The progress made by the Ceramics Branch in the study and fabrication of uncooled rocket nozzles has led to the award of a new contract by the Bureau of Ordnance, Department of the Navy, for the evaluation of slip cast fused silica as a rocket nozzle material for solid propellant rockets. Of particular interest is the fact that this project has allowed us to take advantage of existing bunkers, barricades and magazines to provide a facility for the test firing of solid propellants for the evaluation of rocket nozzles.

A further result of increased support by the Bureau of Ordnance is the acquisition of a plasma jet unit which will allow us to produce, for extended periods of time, temperatures in the range of 15,000 to 25,000° F. As a research tool this will provide information in the fields of flame-sprayed refractory materials as well as the aerodynamic heating of reentry bodies.

In reviewing the past year's work, it becomes very clear that much of our growth and expansion has resulted from the recognition of the value of a material which was originally studied for an industrial sponsor. The Glasrock Corporation, formerly the North Foundry Mold Co., came to Georgia Tech in August 1956 in search of an economical means of constructing a permanent foundry mold from fused silica. High costs and limited sources of fused silica led the sponsor to consider manufacturing the material himself. The successful results of this effort and the resulting availability of relatively inexpensive fused silica have led to the initiation of numerous studies based on slip cast fused silica. Prior to this accomplishment, fused silica had been by-passed for many applications due to the difficulty in forming large and intricate shapes and/or the high cost of forming the ware from molten silica.

The activity of the Ceramics Branch in the field of slip cast fused silica is ample proof that there still remains work to be done with seemingly "old and tried" materials for those with imagination and an open mind.

Authors Mason, right, and Zenoni, discuss the proposed method for insulating a solid propellant rocket motor casing with fused silica. The project is in the proposal stage.

HIGH TEMPERATURE RESEARCH

During the past year, work in this field has been concentrated in flame sprayed coatings, thermite cermets and rocket nozzles

by C. R. Mason and W. F. Zenoni, Project Directors

One of the bunkers and barricades in Tech's testing area for solid propellants. The area is being used for tests with a small oxyhydrogen motor now located in the bunker.

ENGINEERING EXPERIMENT STATION Project A-212 (sponsored by the Department of the Navy, Bureau of Ordnance) in the past has been concerned with high temperature materials in general. During the past year this work was carried out in three particular areas —flame sprayed coatings, thermitic cermets, and rocket nozzle materials. As of September 1, 1958, the rocket nozzle work was shifted to a new Project, A-409 (also sponsored by BuOrd), and Project A-212 was reorganized toward more basic research.

Project A-212
Thermal Protection Systems

As the speed of vehicles which must move through the earth's atmosphere increases, the temperature caused by friction increases. During the re-entry of long range missiles into the earth's atmosphere, temperatures occur which are well above the melting point of most materials known today. This, however, is a condition lasting for only a few seconds, and such short-time heating may be taken care of by various techniques such as ablation and heat sink systems.

In the future there will be a need for certain parts of special vehicles to withstand high temperatures for much longer periods of time. Although in such cases the temperatures will be somewhat lower than those presently encountered, they will nevertheless be above the safe working temperatures of most known materials, and the usual methods of protection will not hold up for the extended periods of exposure. One solution to such a problem is a cooling system to remove the heat and thus keep the material below its critical temperature.

Determining basic information about cooling or thermal protection systems will be the aim of one phase of the work to be carried out under Project A-212. Fused silica, primarily because of its excellent resistance to thermal shock, has been chosen as the material for this research. The first year's work will consist of gathering data on the basic thermal properties of predominantly fused-silica bodies and determining how these properties may be varied. Tests will be made by placing samples in the exhaust of a small oxyhydrogen rocket motor. These samples will be cooled using various techniques and the performance obtained in these tests will be related to the measured thermal properties.

Coatings

Several techniques are presently in use for applying coatings with high melting points to substrates having much lower melting points. All of these techniques are similar insofar as the basic coating mechanism is concerned, that is, they all consist of spraying molten particles onto the substrate to be coated. For the past two years flame sprayed coatings have been under investigation as part of the high temperature research under Project A-212. These coatings were applied using an oxyacetylene flame-spray gun. Coatings of highly refractory oxides (Al_2O_3, ZrO_2), metals (Al, stainless steel, copper) and mixtures of metals and oxides have been successfully sprayed onto various substrates (metals and ceramics). Coatings were developed which provide oxidation protection to the substrates up to 1700° F. However, all coatings applied in this manner have a significant porosity. Further, many materials cannot be sprayed using oxygen and acetylene because their melting points are higher than this flame temperature.

At the present time a new type of spray system is being obtained which will not have these two drawbacks. The new system utilizes a gas-stabilized electric arc as the heat source for melting the sprayed material. The system provides sufficient temperature (10,000° F and up) and heat flux not only to melt and spray any known material that can be melted, but it also produces a coating that is essentially non-porous. Another feature of the system is the fact that

Continued on Page 8

various stabilizing gases may be used, and a shield of gas surrounds the molten particles until they are relatively cool. Therefore, an inert atmosphere is available for spraying such materials as molybdenum and tungsten which would otherwise oxidize rapidly during spraying. The acquisition of this arc-spray system will open up expansive new areas for research in coatings at the Ceramics Branch.

Thermitic Cermets

The term *cermet* is generally used to describe a material made up of a ceramic and a metal—the mixture having been fired to very high temperatures to obtain a dense, strong, heat resistant material. The word *thermitic* indicates that the cermet, as described above, is formed by the products and heat of a thermite reaction. For example, to form a cermet composed of chromium metal and aluminum oxide, rather than heat a mixture of these two materials to 3000° F or more for several hours, a mixture of aluminum and chromium oxide is heated to only 1800° F and the following reaction takes place:

$$2Al + Cr_2O_3 \longrightarrow 2Cr + Al_2O_3 + \text{heat}$$

Such reactions, using aluminum as the reducer, have been studied during the past three years. The reactions have been controlled to reduce cracking and warping in the final shape, additions have been made to the basic reactants, and intermetallics such as borides and carbides have been formed. Recently thermite reactions have been studied in which beryllium metal was used as the reducer. Such a reaction, similar to the aluminum reaction above, would be:

$$3Be + Cr_2O_3 \longrightarrow 3BeO + 2Cr + \text{heat}$$

Thermitic cermets formed using a beryllium thermite reaction have several possible advantages. BeO rather than Al_2O_3 is one of the products. BeO is less dense, has a higher melting point and has greater resistance to thermal shock than Al_2O_3. Thus far, the following oxides have been observed to be reduced by beryllium:

Cr_2O_3, ZrO_2, Al_2O_3, WO_3, and TiO_2.

Presently the reaction with Cr_2O_3 is being studied more closely with regard to controlling the reaction to obtain a dense, fault-free body.

Project A-409

All of the testing to date on rocket nozzle inserts has been concerned with dry-pressed inserts. These inserts were composed primarily of fused silica and were evaluated using a small oxyhydrogen rocket motor. Several attempts have been made to scale up these small dry-pressed inserts for testing in larger solid fuel motors. The nature of the dry-press process, however, does not lend itself to the fabrication of these larger shapes; and while these larger inserts were not complete failures, it was felt that the quality of the smaller inserts could not be approached in larger inserts using the dry-press technique. Therefore, with the initiation of Project A-409, all nozzle inserts will be fabricated utilizing the slip casting process. This process lends itself equally well to the fabrication of small and of large shapes.

The small oxyhydrogen motor will be used for screening a wide variety of slip cast compositions. This motor provides an inexpensive, rapid test for resistance to thermal shock and high temperature erosion. In addition to this screening test, a facility for testing larger inserts in a solid fuel motor is near completion. This test will be used for testing only compositions that perform well in the screening tests on the small motor. The tests on the solid fuel motor are necessary to determine the erosion effects of the products of composition of solid fuels on inserts of various compositions. Insert compositions which look promising after being tested on both of the motors at the Ceramics Branch will then be tested by other agencies in larger motors using fuels of various compositions.

by Nick Poulos, Research Engineer

CLAY MINERAL RESEARCH

SEVERAL YEARS AGO, the Georgia Tech Engineering Experiment Station initiated a project to study Georgia's principal mineral, kaolin. As a result of continuing interest in this project, Georgia Tech now has clay research facilities which excel any other institution in the Southeast. Several of the clay producers of Georgia have sponsored or are sponsoring further studies at the Station, utilizing the facilities for both fundamental and applied research in clay minerals.

Tech's facilities for this work include up-to-date ceramic and optic labs, and equipment for electron microscopy, electron diffraction, X-ray diffraction, differential thermal analysis, surface area determination and other general lab equipment such as pH meters, viscosimeters, particle size determination apparatus and high temperature fusion apparatus.

Such capabilities make it possible to discover subtle properties that might otherwise remain hidden in the clay compounds. For example, suppose a kaolin from deposit A is a good coating clay, and a kaolin from deposit B is not, but both clays appear to be identical outwardly. The use of the electron microscope may indicate the minute differences between these two clays, and this knowledge could possibly lead to a method of processing the B clay to change it to a good commercial coating clay.

In the spring of 1958, the Ceramics Branch set up a new project (E-177-1) using State funds to study the feasibility of forming a synthetic ball clay from a suitable kaolin.

One of the primary uses for ball clays is in the production of ceramic whitewares such as chinaware, sanitary fixtures, wall and floor tile, and electrical insulators.

Ball clay is used in whiteware bodies because it enhances the workability of the body. This enhancement is due to the rheological properties of high plasticity and excellent suspending action. Although these properties make ball clay a necessary constituent of whitewares, particularly whenever the whiteware is slip cast, ball clays exhibit some undesirable qualities such as:

1. Excessive organic matter, causing difficulties in glazing and firing of a ceramic whiteware.
2. Lack of uniformity; deposits are highly stratified and variable. Deposits are relatively small and it is usually necessary to blend two or more sources in order to maintain a semblance of uniformity.
3. The presence of inorganic impurities such as ferric oxide and titanium dioxide. These impurities affect the whiteness of the fired body.
4. High cost; the nature of the deposits makes efficient mining impossible.

It is generally felt that a ball clay that did not exhibit these undesirable qualities would be greatly desired by its users, but it is doubtful if such a ball clay could be found in nature. However, such a clay could possibly be produced synthetically from a suitable kaolin.

The work on synthetic ball clays has been primarily devoted to evaluating Georgia kaolins, which were supplied by the various kaolin producers in the State. The standard physical properties were determined, and ceramic body slips were made using the most promising kaolin as the ball clay substitute. The kaolin used was treated with additives that were thought to improve its physical properties to that of a well known ball clay. Ware was cast using these slips. Casting rate, strength, shrinkage, tearing and gelling of the slips were determined.

This preliminary work has indicated that the forming of a synthetic ball clay from kaolin is feasible. However, considerable work is needed before this becomes a reality.

CERAMIC NOSE CONES

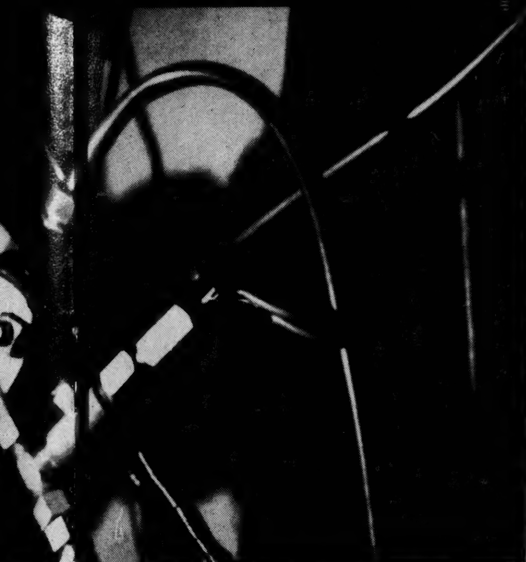
Ceramic materials show great promise in solving one of man's most vexing problems — how to return a rocket payload intact

With the launching of Russia's sputnik heralding the sudden arrival of the Space Age in the fall of 1957, the importance of many scientific and engineering problems jumped to matters of great national concern. The greatest of these have been connected with the development of intercontinental ballistic missiles—and in this development ceramic materials are expected to play a vital role.

To propel a vehicle into space is one problem, but to get a vehicle into space and return its payload intact is quite another matter. The problem becomes difficult due to what rocket developers term re-entry, the return of the missile from relatively airless space to the thicker air near the earth. The velocities attained by a rocket upon re-entry into the earth's atmosphere are reported to be as high as 15,000 miles per hour. The temperatures developed on the nose of the rocket under these conditions may reach 4000 - 5000° F. Similar conditions exist when a falling star enters our atmosphere and the burning of the star allows us to see it. In the case of a star, the burning reduces it in size until only a fraction of the original mass hits the earth, and thus the earth's atmosphere acts as a protective shield. But in the case of our rockets, it is essential that they return to the earth with little or no damage.

Station Project A-330 (sponsored by U. S. Army Ordnance, Redstone, Alabama, under Contract No. DA-01-009-ORD-548) which was begun April 1, 1957, has been concerned with the development of materials for resistance to high velocity erosion at high temperatures.

The work carried out during the past



A fused silica nose cone model is subjected to rigorous tests in a rocket motor exhaust.

by Nick Poulos, Research Engineer

year was primarily devoted to two phases, (1) basic studies of ceramic body compositions and (2) fabrication of nose cones from the most promising ceramic body composition developed in phase one.

The prime requisite for a ceramic nose cone material is that it must withstand a sudden or instant heating from a relatively low temperature to a very high temperature, i.e., from 32° F to 2000° F in a few seconds, without failing. Most ceramic materials fail drastically upon being subjected to this extreme thermal shock; however, fused silica can withstand such shock without failing. Therefore, it was selected for use as the basic ceramic nose cone material.

The fused silica used in this case was in the form of a slip, finely divided particles suspended in some medium such as water. Suitable shapes can be cast in plaster molds using such a slip. This is a conventional ceramic forming technique which has been used for many years.

Basic Body Compositions

Emphasis has been placed primarily on increasing the strength of the slip cast fused silica. The effects of grain size distribution, firing time, temperatures and firing procedure on the strength of the slip cast fused silica were investigated. Another approach to improving the strength was by an additive such as phosphorous pentoxide. This addition was accomplished by soaking the cast silica in phosphoric acid and then firing the soaked ware to 1800° F. Transverse strengths in excess of 7000 psi have been obtained by the methods mentioned above.

Another approach to improve the strength of the basic nose cone body is by resin impregnation. The resin serves a dual purpose. It strengthens the body and it acts as a coolant by its burning and/or vaporizing out of the basic skeleton structure of the fused silica body as the nose cone is subjected to the extreme heats resulting from re-entry. Induced, controlled porosity in the slip cast fused silica was accomplished by suspending suitable materials having a desired particle size and which could be burned out during the firing operation. The resulting porous structure was impregnated with an organic resin by vacuum-pressure techniques.

Other body compositions such as graded cross-section and heterogenous mixtures have been evaluated with promising results.

Nose Cone Fabrication

Nose cone shells exhibiting good strengths, excellent thermal shock resistance, and excellent dimensional stability have been cast in plaster molds using fused silica slips.

Large shapes have been cast with little difficulty and it appears as though any size can be easily fabricated by the slip casting technique.

FUSED SILICA FOR REACTORS

by J. D. Fleming, Project Director

FOR MANY YEARS, the primary interest in nuclear reactors has been as a source of steam for the generation of electrical power. Although the generation of electrical power is of importance, especially in remote regions, a far more extensive use of nuclear reactors for industrial heat is indicated for the future.

Of the total energy produced in America today, over 80 per cent is used directly as heat. Only about 20 per cent of the energy produced is converted to electricity. This indicates that a major nuclear field, that of process heat generation, is yet to be fully explored. This field would include specific applications such as space heating, low quality process steam generation, thermal cracking of hydrocarbons in the gasoline industry, pyrometallurgical processing, ore refining, and aircraft nuclear propulsion.

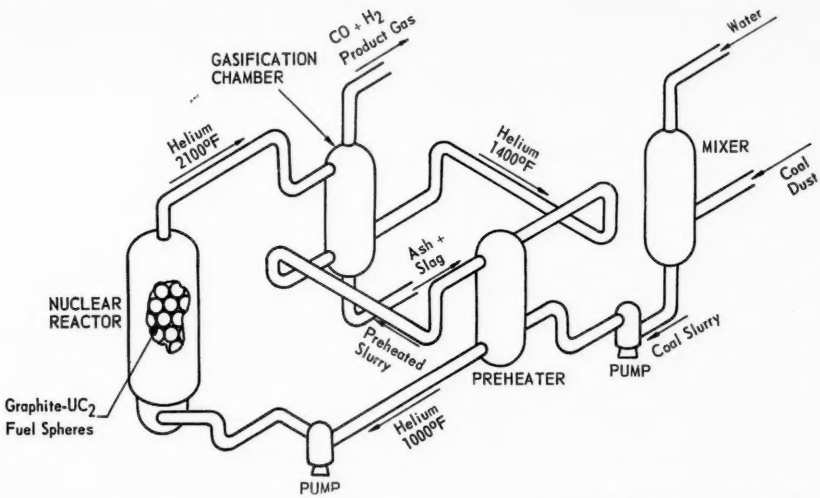
In the generation of steam for electrical energy production, the temperatures of operation of the reactors have been low, usually less than the critical temperature of water (705° F). This restriction on the operating temperature level has led to poor thermal efficiencies. However, these low temperatures have permitted use of more conventional structural materials such as metals.

With the advent of high-temperature, process heat reactor studies, the thermal efficiencies have increased at the expense of much more severe material requirements. Metals such as the stainless steels, aluminum, zirconium, and even uranium, which have been extensively used in low temperature reactors, cannot serve in high temperature reactors because of low melting points, low creep strengths, or phase changes. Ceramic materials, with their better high-temperature properties, will thus be called upon to play a more important role in process heat reactors.

Because of its low thermal expansion, excellent nuclear properties, and ease of fabrication (by techniques developed at the Engineering Experiment Station), fused silica has attracted interest as a possible material for use in high-temperature reactors. This interest has culminated in the award to the Station of an Atomic Energy Commission contract intended to explore the nuclear applications of fused silica.

The new project, B-153, is primarily directed towards the basic study of fused silica with emphasis on the determination of the properties that would characterize its value as a reactor material. Of obvious importance is the investigation of the high-temperature strength of the fused silica. This will be determined by the measurement of short-time ultimate tensile strengths and compressive strengths at elevated temperatures.

In addition to the ordinary strength parameters, information will be required on the effects of irradiation on these parameters. Since fused silica is already in the amorphous state, less damage would be expected from its irradiation than is normally observed in the irradiation of crystalline materials. Furthermore, since silica is primarily ionic, the amount of damage would be expected to decrease with increasing temperature. Although these predictions have been supported to some extent by x-ray diffraction investigations, little work has been done on the effect of irradiation on the physical properties of fused silica.



The conceptual design of the type of reactor in which fused silica heat exchanger may be used. The study of the use of fused silica for reactors has just started here.

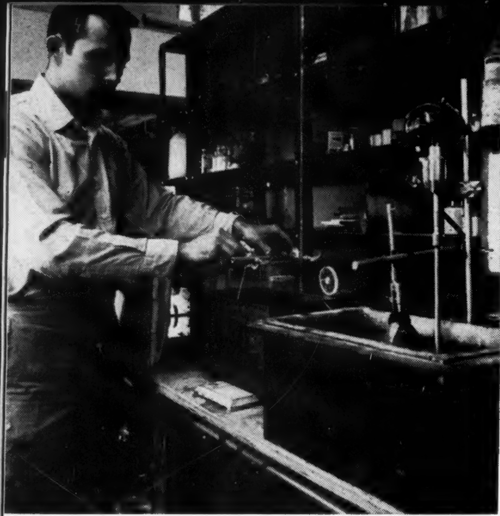
In Project B-153, fused silica tensile test specimens will be subjected to in-pile irradiation (at off-campus facilities until Tech's reactor is operational in 1960). After irradiation to predetermined extents, the samples will be returned to the laboratory for testing.

Fused silica is known to devitrify under normal conditions at approximately 2100° F. The normal effect of irradiation on materials is the generation of amorphous areas because of ionic or molecular displacement. It is possible, then, that one influence of irradiation on fused silica will be an increase in the temperature necessary to cause devitrification because of the continuous formation of the amorphous regions.

Another facet of Project B-153, therefore, will be the study of the vitrification of crystalline silica, as cristobalite, caused by irradiation. Devitrification rates of fused silica will also be studied, using a high-temperature x-ray camera, by the Engineering Experiment Station X-ray Laboratory. The comparison of the vitrification rate with this devitrification rate will serve as a basis for estimating the useful temperature range of fused silica in the presence of high-level radiation.

Gaseous heat transfer media have been proposed for use in high temperature process heat reactors. Gases also make up about 13 per cent by weight of the fission products formed in reactor fuel elements. In evaluating fused silica for use in heat transfer systems for gaseous coolants and in fuel matrices, information will be required on the resistance of the silica to permeation by gases. Permeation rates will be determined using tracer techniques with krypton and xenon. Attempts will be made to improve the permeation resistance of the fused silica by heat and chemical sealing techniques.

In addition to these more basic studies, the Engineering Experiment Station has been requested, as a part of Project B-153, to fabricate shell and tube heat exchangers from fused silica. These exchangers are to be tested by the Bureau of Mines for use in their coal gasification reactor now under construction in Morgantown, West Virginia.



Former Tech fullback, Dick Mattison, now an Emory medical student working part-time at the Station, works with the apparatus which continuously coats wire with a Tech-developed high-temperature insulation.

High Temperature Electrical Insulation

by Joe Harris, Project Director

EVER-INCREASING SPEEDS and temperatures not only threaten the skins of missiles and aircraft, but also place severe requirements upon the vital electronic components inside them. On February 1, 1957, a project was initiated at the Engineering Experiment Station to develop high temperature electrical insulation material for copper wire, capable of withstanding temperatures up to 1500° F. This research is supported in whole or in part by the United States Air Force under Contract AF-33(616)-3944 and monitored by the Materials Laboratory, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio. The electrical properties required for this insulating coating include high dielectric strength, low loss tangent, and low dielectric constant. The physical properties required are operating temperatures of -85° F to 1500° F, flexibility, abrasion resistance, thermal shock resistance and corrosion resistance.

The use of ceramics became imperative because of the temperature and electrical requirements. Ordinarily, ceramics have very little flexibility. Some glass or porcelain enamel coatings have been used previously and have achieved some degree of flexibility by being applied in very thin coatings. It was felt that it would be very difficult to meet contract specifications with a coating of this type because (1) the enamel would have to be applied in a very thin coating, and chances of having pinholes in the coating would be very great, (2) the thinness of the coating would limit its dielectric strength, and (3) glasses tend to become conductors as they approach their melting point, requiring that a glass coating would have to be applied at a temperature much greater than would be encountered in service.

The need for flexibility of a wire insulation would be during installation at room temperature; once installed there would be no further need for flexibility. Tech's approach, as outlined in the October, 1957, issue of this publication, was to combine an organic and an inorganic coating in the form of a resin with a powdered glass filler, the resin providing the necessary initial flexibility. Once this insulation system is heated up, the resin should burn out and the powdered glass filler should fuse forming a continuous coating to 1500° F. But a glass that will fuse at the burn-out temperature of the resin will be in a viscous liquid state at 1500° F and would act as a conductor. The attempt to solve this problem was to use a non-fusing porous

base coating and to apply the resin-glass enamel coating over the base coating as a sealer against moisture.

The best base coating thus far obtained has been aluminum oxide, obtained by anodizing a layer of aluminum over the copper base metal.

Satisfactory coatings of aluminum on copper have been obtained by electroplating in an anhydrous ethereal solution of lithium aluminum hydride. This process was described in the October, 1957, article also. It is felt that in production it would be impossible to completely anodize all of the aluminum. The diffusion of aluminum in copper at elevated temperatures, therefore, presents a problem because a small amount of aluminum in copper drastically reduces its electrical conductivity.

Work was next directed towards applying aluminum to copper coated with a barrier layer, a metal that would prevent the diffusion of aluminum into the copper at elevated temperatures. Efforts were made to plate aluminum on substrates of chrome and iron electroplated on copper, and also on an inconel-clad copper wire. None of the coatings obtained could be anodized due to discontinuities in the aluminum coating.

At least two companies are now working on the problem of cladding copper wire with aluminum. One company is approaching the problem by applying a barrier layer metal (silver) to a copper rod or wire by electroplating, and then inserting the plated copper rod into an extruded tube of aluminum; the composite rod is then swaged and reduced by drawing.

Since these companies are directing major efforts toward perfecting aluminum-clad copper wire, it was decided that Tech's efforts would be directed toward the anodizing and sealing of the wire; aluminum-clad copper wire would be obtained when it becomes available. Work has thus far been progressing by anodizing 2 S aluminum wire and applying the sealing resin-glass coatings to this wire. The anodized aluminum wire has great flexibility—it can be bent around a mandrel only ten times the diameter of the wire without crazing or cracking. Wires with resin-glass sealing coatings are now being tested for electrical and physical properties up to 1100° F (limited by the melting point of aluminum).

Another system now being investigated makes use of an inorganic oxide sealer for the aluminum oxide coatings, thus eliminating the resin-enamel glass sealing coatings. This system involves the sealing or impregnation of the porous anodized coating with colloidal silica.

Charged particles suspended in a liquid will move toward the pole of opposite charge if a potential is applied across the system. This process is known as electrophoresis. Colloidal silica is negatively charged. Therefore, by placing the anodized wire in an organic dispersion of colloidal silica as the anode, supplying a suitable cathode, and applying a potential across the system, the particles of silica can be made to migrate to the anode. Preliminary electrical data obtained for aluminum oxide coatings sealed in this manner indicate this type of coating is superior to glass coatings.

Since aluminum oxide crystals are long, columnar crystals with pore openings between them, this type coating obtains its flexibility from the ability of these crystals to move in the space of these pore openings. Therefore, the colloidal silica must be deposited as a thin film and not completely clog the pore openings. Attempts are now being made to deposit an amount of silica to obtain optimum electrical properties and to still retain flexibility. It is felt that a wire system is now available which would require only a minor development effort to be used for a "one-shot" operation between room temperature and 1500° F. Such a wire would have an anodized film sealed with a suitable resin to prevent moisture pick-up. On heating to 1500° F, the resin would burn out, but the moisture problem would then be nonexistent anyway.

PORCELAIN ENAMELED STEEL PLATE

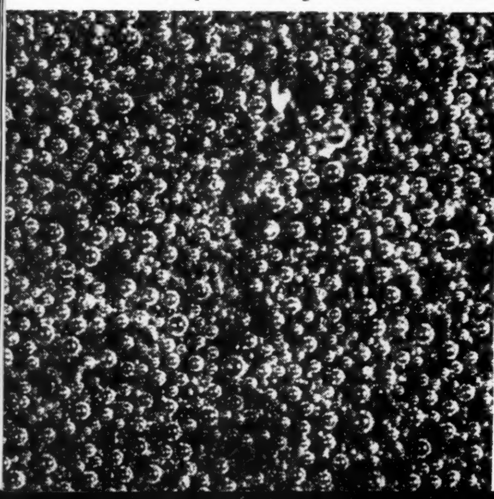
by Joe Harris, Project Director

MARINE EXHAUST MUFFLERS, snorkel tubes and other shipboard components are frequently porcelain enameled for protection from corrosion. In the event of a national emergency, the common metals that might be available in plate thickness such as rimmed, killed and semi-killed steel, may cause many defects in porcelain enamel coatings applied to them.

The determination of factors affecting the enameling characteristics of steel plate and the development of a complete and technically accurate description of steel plate that is acceptably receptive to porcelain enamel coatings are the objectives of Station Project A-413, which is a continuation of the work begun under Station Projects A-308 and A-204. The first phase of this work was reported in the October, 1957, issue of this publication.

Porcelain enamel, a glass coating fused to metal, has a texture between that of a flat paint and a smooth glass. The first step in the basic process of making porcelain enamels is to melt the raw materials to form the desired glass.

Photomicrograph of porcelain enamel coating on steel plate showing desired bubble film.



Enamel glasses are of borosilicate type. The raw materials for the glass are essentially all inorganic oxides, mineral fluorides or salts, varying from granular to powdered in form. The glass composition is weighed out in the established proportions and thoroughly mixed. The mixture of materials is melted at temperatures of 2000° to 2600° F. When the melting is complete, the molten glass is poured into a tank of water to break the glass up into a friable condition known as frit.

The frit is then ground in a ball mill along with water, clay and electrolytes (inorganic salts) to form a water suspension, or slip. After first cleaning the metal by sand blasting or acid pickling, the porcelain enamel slip is applied to the metal by dipping, spraying or other techniques. The operation is completed by drying the water out of the coating and firing until the glass fuses to the desired degree, usually in the temperature range of 1300° to 1700° F.

The most common defect encountered in enameling steel plate—of the type to be used in ships—is fishscaling. Fishscaling is the spontaneous fracturing of the glassy coating, exposing the metal underneath. The defect is usually shaped like a fishscale, hence the name. Fishscaling may not show up for days or weeks and often the enameled article is put into service in this potentially defective condition.

Fishscaling has been attributed to gases occluded by the steel which are subsequently precipitated at the enamel-metal interface after the enamel has cooled. Analysis of the gases collected indicate that hydrogen is the most abundant gas present. The hydrogen apparently is injected into the steel at enameling temperatures by the reaction between the

steel and the chemically combined water in the frit.

A hydrogen extraction apparatus has been developed to measure the amount of gas injected into the steel under various enameling conditions and with the use of various enamels. By observing the tendency of an enameled plate to fishscale in comparison with the amount of gas extracted from a metal blank which has been coated with enamel and fired under the same conditions, a correlation may be found between the amount of hydrogen occluded and the tendency to fishscale. Previous work on this project has shown that commercial enameling clays and porcelain enamel frits are not consistent from batch to batch. Also commercial porcelain enamel frit manufacturers may change their frits from time to time. Part of the work under Project A-413 will be devoted to the development of a "reagent frit" to be used in conjunction with the development of a "reagent enamel." This reagent frit will be formulated and smelted under closely controlled laboratory conditions to make each batch as consistent as possible.

As was pointed out in the article last year, a relationship exists between the structure of an enamel called the bubble film and its tendency to fishscale. An enamel that has large uniform bubbles closely spaced has less tendency to fishscale than an enamel with small, poorly defined bubbles. This may be attributed to the fact that the large bubbles provide collection chambers for the hydrogen and/or the large film area provides a stress relief area.

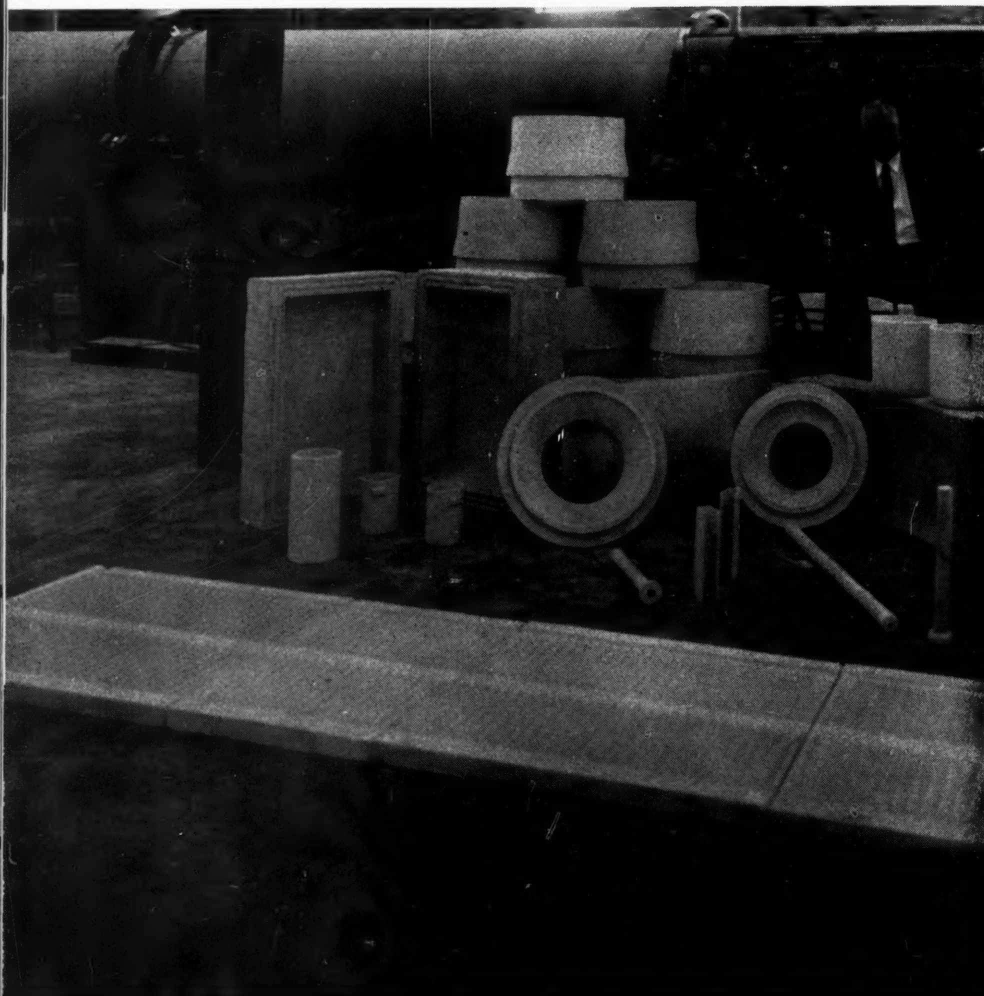
The condition of the bubble film in an enamel depends on many variables such as firing time and temperature. One of the major variables in the formation of bubble film is the type of clay used in the mill batch. Unfortunately, clays are naturally occurring (although some clays go through several processes before they are ready for use as enameling clays). Therefore, they cannot be as closely controlled as reagents synthesized in the laboratory. In the Tech research, a number of commercial enameling clays will be obtained. And each batch will be evaluated by milling with the reagent frit and electrolytes, and applying this slip to steel plate and firing under controlled conditions. The clays producing well-formed bubble films will be examined for such parameters as (1) particle size and shape, and (2) organic and water content. The appartus used in this study will be differential thermal analysis equipment, microscopes and other optical equipment, and possibly the electron microscope.

Work under the previous two projects on porcelain-enameling steel plate has shown that additions of aluminum oxide to the mill batch greatly improves adherence, thermal shock resistance, and resistance to fishscaling. It is thought that this material acts in the same manner as the bubble film to eliminate fishscaling tendencies. Fused aluminum oxide in a variety of particle sizes will be obtained and added to mill batches of reagent enamel. This alumina-bearing enamel will be subjected to proof test by application to steel plate. Any fishscaling tendencies can be accelerated by heating the steel plates to 175° C and holding for 24 hours.

The reagent enamel with and without additives of aluminum oxide should be as free from fishscaling tendencies as possible. A large number of steel samples with as much variation as possible will be obtained. Sample plates of each steel will be coated and fired with the reagent enamel with and without mill additions of aluminum oxide. A metal blank of each sample will be prepared and gas extraction data obtained. Attempts will be made to gain a correlation and to set standards for an acceptable amount of gas to be obtained from a metal blank coated with a reagent enamel and fired under standard conditions. It is anticipated that this procedure will provide a satisfactory method for establishing standards for enameling quality steel.

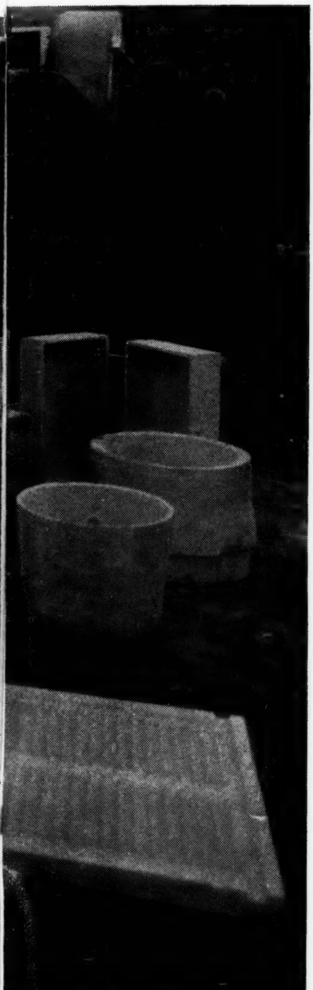
The work that resulted in the development of a material for nose cones also has industrial uses

Tom North, vice president in charge of sales for the Glasrock Company and some of the various fused silica items which are now being manufactured by this new company.



INDUSTRIAL USES OF FUSED SILICA

by John North, President of Glasrock Corporation



THE CERAMICS BRANCH has developed various forming and bonding techniques for fused silica under the sponsorship of the Glasrock Corporation. The Branch has also been able to suggest promising areas for development both in methods of fabrication and in possible uses. The industrial sponsorship is continuing. The Station is collaborating in the projection and evaluation of new ideas and techniques, and the solution of problems that crop up as the sponsor produces trial and production run pieces for commercial use.

Glasrock is producing many large and small shapes wherever a need is found for a thermal-shock-resistant ceramic or for large ceramic shapes to resist acids and chemical fumes.

The low thermal expansion of the rebonded fused silica makes it practically immune to thermal shock and to the thermal stresses usually set up in the firing of ceramic ware. This accounts for one of the unique applications—the manufacture of fired ceramic bodies of unlimited size which are crack-free and dependable in structural strength while unsupported by metal or brick back-up or reinforcement.

Glasrock Corporation has manufactured ceramic blocks approximately 6 feet square by 11 inches thick, free of warping or cracks, and with smooth-surfaced cavities. Much larger pieces are contemplated in the near future, and there seems to be no practical limit to the sizes that can be produced with simple and inexpensive equipment.

Applications are being investigated in many fields. The results of various trials will be announced by the sponsor as developments warrant.

Edited In Retrospect

About this issue

• *The Research Engineer's* October, 1957, issue on ceramics was prompted by the explosive growth of Georgia Tech's ceramics research group (the Ceramics Branch) during that year. We thought that this was a good story, one worthy of a special report. But even our prejudiced interest was caught short by the unprecedented demand for extra copies of that particular issue. We received as many as 100 requests for it in one week, and in a short time our entire supply was exhausted.

Because of the many requests for this issue that we have been unable to fill, and because of the increased importance of Tech's research work in this field, we feel that it is about time to devote another full issue to ceramics research at Georgia Tech. In fact, the activity of the Ceramics Branch has reached such a high level and is attracting such national attention that we are considering making this special issue an annual feature.

The Special issue

• This thought brings up one of those little problems that constantly plague editors but probably go unnoticed by the readership: Is it proper to have more "special" than "regular" issues of any magazine? With the annual research report, the annual nuclear science issue, a ceramics report, and an occasional special issue like the one in July on Textiles, *The Research Engineer* will soon have more "specials" than there are issues in a year. But then, this magazine is ideally suited to special issues on one subject. Probably the best solution is just to give them other labels, as we have done with this *Follow-up Report on Ceramics.*

The new schedule

• As you have probably noticed this is the fifth issue of *The Research Engineer* for 1958, and the second one under our new publication schedule. The magazine will in the future reach you five times each year in February, April, June, October and December, a plan that supersedes the one announced in the past July issue.

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